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(54) [Title of the Invention] Nitrogen Trifluoride Exhaust Gas Treatment Method and Apparatus

[Limits of the Patent Claims]

[Claim 1] A method for treatment of NF_3 exhaust gas;

wherein an exhaust gas that contains at least NF_3 undergoes thermal oxidative decomposition; and the NF_3 oxidative decomposition products and / or derivatives thereof react with NH_3 .

[Claim 2] An apparatus for treatment of NF_3 exhaust gas;

wherein the apparatus comprises a thermal oxidative decomposition apparatus that has a reactor that causes an exhaust gas that contains at least NF_3 to undergo thermal oxidative decomposition; and the reactor reacts NH_3 with NF_3 oxidative decomposition products and / or derivatives thereof.

[Detailed Explanation of the Invention]**[0001]**

[Industrial Field of Application] The present invention relates to a method and apparatus for detoxification by cleaning of NF_3 exhaust gas that is generated by the semiconductor, liquid crystal, etc. manufacturing fields.

[0002]

[Prior Art] When NF_3 is used for cleaning of semiconductor and liquid crystal manufacturing CVD equipment, as much as 50% of the NF_3 is discharged unreacted.

[0003] Various methods exist for the removal of NF_3 . These NF_3 removal methods include: contacting NF_3 with heated silicon particles, conversion of NF_3 to SiF_4 , followed by adsorption of SiF_4 upon an immobilized alkaline material; contacting NF_3 with heated carbon granules so that NF_3 converts to CF_4 ; and the like.

[0004] Although these methods are effective for the removal of NF_3 alone, these methods have the following deficiencies. The method that uses contact with silicon particles generates NO_x when the exhaust gas contains oxygen. The method that uses contact with carbon granules discharges CF_4 (a type of Freon compound), and the carbon granules are consumed by reaction with oxygen when the treatment gas contains oxygen.

[0005] Furthermore, each of the methods requires additional treatment to remove toxic components (SiF_4 , NO_x) within the cleaning exhaust gas, thereby raising costs.

[0006]

[Problems to be Solved by the Invention] By the use of a thermal oxidative decomposition apparatus that is also effective for treatment of CVD exhaust gas during CVD utilizing SiH_4 , TEOS, etc., NF_3 -containing cleaning exhaust gas treatment can be carried out while reducing equipment cost. When the NF_3 undergoes thermal oxidative decomposition, F_2 and NO_x are formed by decomposition above 800 °C. Although F_2 and SiF_4 within the cleaning exhaust gas are removed by water scrubbing, NO_x is discharged in the final exhaust since removal of NO_x by water scrubbing is inefficient. Problems arise due to generation of NO_x and the corrosion resulting from acidity of the scrubbing water.

[0007] The goal of the present invention is to provide a method and apparatus for NF_3 exhaust gas treatment that has low operational cost, that eliminates NO_x , and that can effectively prevent equipment corrosion.

[0008]

[Means to Solve the Problems] The present invention comprises the (1) method and the (2) apparatus described below, thereby making possible solution of the above mentioned problems.

(1) A method for treatment of NF_3 exhaust gas; wherein an exhaust gas that contains at least NF_3 undergoes thermal oxidative decomposition; and the NF_3 oxidative decomposition products and / or derivatives thereof react with NH_3 .

(2) An apparatus for treatment of NF_3 exhaust gas; wherein the apparatus comprises a thermal oxidative decomposition apparatus that has a reactor that causes an exhaust gas that contains at least NF_3 to undergo thermal oxidative decomposition; and the reactor reacts NH_3 with NF_3 oxidative decomposition products and / or derivatives thereof.

[0009] For the present invention, NF_3 -containing exhaust gas or NF_3 exhaust gas (referred to below simple as "exhaust gas") is a gas that contains NF_3 . Such exhaust gas is taken to be the exhaust gas of an apparatus (such as would be used for semiconductor manufacturing) that utilizes cleaning gas that contains at least NF_3 . Such exhaust gas is taken to mean an exhaust gas that contains process gases and reaction products (derived from reactions between NF_3 and substances to be cleaned within the apparatus during cleaning treatment using cleaning gas). Therefore the NF_3 detoxification treatment of the present invention is taken to include removal of NF_3 derivatives.

[0010] The present invention, by thermal oxidative decomposition of exhaust gas, converts organic components in the process-derived exhaust gas into water and CO_2 , and inorganic components are converted into SiO_2 , etc. metal oxide fine particles. These components are removed by water scrubbing, etc. as desired. At the same time, the NF_3 , etc. to be removed is converted into NO_x , HF, etc., and this NO_x and HF are reacted with NH_3 , thereby obtaining a NF_3 -detoxified cleaned gas.

[0011] Per the present invention, NH_3 reacts with the NF_3 thermal oxidative decomposition substances and derivatives thereof. In addition, residual NH_3 can react with substances (generated by the thermal oxidative decomposition treatment and derivatives thereof) that are reactive with NH_3 , such as residual SiF_4 and H_2O in the cleaning gas.

[0012] Moreover, use of an excessive quantity of NH_3 gas is not a problem since NH_3 is removed by water scrubbing, etc. Since the use of an excess of inexpensive NH_3 gas is harmless, corrosion is prevented, equipment costs decrease, and operational costs can be reduced relative to the prior art (final-stage removal of NO_x).

[0013] An example that can be suggested of the apparatus that discharges exhaust gas of the present invention is a CVD apparatus. The exhaust gas comprises CVD exhaust gas derived from CVD treatment process gas and / or cleaning exhaust gas during cleaning treatment.

[0014] Examples of the process gas included in such CVD exhaust gas include inorganic raw materials (such as monosilane, disilane, dichlorosilane, etc.) and organic raw materials (such as TEOS (tetraethoxysilane), TMB (trimethoxyborane), etc.), used either a single substance or as a mixture thereof. The CVD exhaust gas includes such unreacted gases, derivatives thereof, and decomposition reaction products {such as H_2 , CO , alcohols ($\text{C}_2\text{H}_5\text{OH}$, etc.), aldehydes (CH_3CHO , etc.), and hydrocarbons (C_2H_4 , etc.)}. The major components are metal oxides (such as SiO_2 , etc.), H_2O , and CO_2 . Here the meaning of thermal oxidative decomposition includes simple oxidation of non-decomposable compounds (such as hydrogen) and oxidation, etc. of metallic, etc. elements. [TRANSLATOR'S NOTE: The chemical name normally cited as TMB is trimethylborate. "Trimethoxyborane" sounds rather odd.]

[0015] This cleaning exhaust gas comprises at least NF_3 . This cleaning exhaust gas can also comprise reaction products of NF_3 and substances (non-exhausted CVD treatment reagents, etc.) within the CVD apparatus (such as SiF_4 , NF_3 derivatives), cleaning gas, and CVD internal substances physically removed by the cleaning gas.

[0016] Examples that can be suggested of the cleaning gas include CF_4 , C_2F_6 , SF_6 , ClF_3 , etc. For the present invention no particular limitations are placed upon the means used for reacting NH_3 with thermal oxidative decomposition products of NF_3 and / or derivatives thereof. Any method can be used as long as the reaction between NH_3 and reaction product compounds (HF , NO_x , etc.) is accomplished. Specifically, NH_3 is added and mixed with exhaust gas prior to thermal oxidative decomposition. It is also permissible for NH_3 to also be added simultaneously with the exhaust gas thermal oxidative decomposition reaction and / or thereafter.

[0017] NH_3 may be added simply as NH_3 gas or in another form, such as a gas mixture with air, etc. The quantity of NH_3 used is proportional to the quantity of oxidative decomposition products and / or derivatives thereof. Normally the preferred quantity is at least 4 moles of NH_3 per 1 mole of NF_3 in the exhaust gas.

[0018] No particular limitations are placed upon reaction conditions of the thermal oxidative decomposition treatment of the exhaust gas components and exhaust gas feed conditions, etc. of the present invention as long as such conditions are sufficient for the above mentioned reactions with NH_3 . Thermal oxidative decomposition may be carried out upon those substances within the exhaust gas at least capable of undergoing thermal oxidative decomposition in the presence of oxygen. Therefore, oxygen must exist within the reactor as the exhaust gas is fed to the reactor. Although the method by which oxygen is made to exist within the reactor is arbitrary, a preferred method is to feed oxygen-containing gas (such as air, etc.) together with the normal exhaust gas. Furthermore, an arbitrary gas can co-exist with the exhaust in order to adjust conditions of the thermal oxidative decomposition. For example, an inert gas (nitrogen, etc.) is preferably mixed with the exhaust gas so that the exhaust gas is enveloped by such nitrogen gas that is itself enveloped by oxygen, thereby forming a three-layered gas stream that is fed to the reactor of the thermal oxidative decomposition apparatus. The gas feed lines of the thermal oxidative decomposition apparatus preferably have a three-layered concentric structure. When this type of gas feed line structure is used, NH_3 gas may be fed by addition to the normal exhaust gas, or alternatively, by addition to the nitrogen gas or air, etc.

[0019] Furthermore, although the heating means used for thermal oxidative decomposition is arbitrary, a preferred heating means is a temperature-controlled electrical heater which can be provided at the interior wall of a normal reactor. Moreover, the preferred reaction temperature range is 800 to 1000 °C.

[0020] The exhaust gas (referred to below as treated gas), that has undergone thermal oxidative decomposition and / or reaction with NH_3 per the present invention, according to the composition of the treated gas, can be discharged to the environment or can undergo additional arbitrary treatment.

[0021] In particular, a preferred treatment of the treated gas is contact with water, specifically water scrubbing treatment. Metal oxide fine particles (SiO_2 , etc.) generated by the decomposition treatment are captured and removed by this means, and water soluble compounds (SiF_4 , F_2 , etc.) are removed by dissolution and NH_3 neutralization. Water scrubbing treatment also can cool the treated gas. The type of water scrubbing treatment is arbitrary, although the preferred method is contacting the treated gas with a spray.

[0022] Water scrubbing of the treated gas can be performed by equipment external to the thermal oxidative decomposition apparatus, although this equipment is preferably united (constructed as a single unit) with the thermal oxidative decomposition apparatus as per the present invention. The reactor quite preferably comprises an initial gaseous reactor stage (for thermal oxidative decomposition) and a final water scrubber (for neutralization reaction with NH_3).

[0023] After water scrubbing treatment of the treated gas, the post-water-scrubbing treated gas can be discharged to the environment or can undergo additional arbitrary treatment, such as known adsorption, etc. treatments, and arbitrary exhaust means can be used (such as an exhaust pipe, etc.). Furthermore, the water scrubbing waste water can be discharged from the system by a discharge line, etc., or alternatively, this waste water can undergo additional treatment. The thermal oxidative decomposition apparatus can be equipped (constructed as a single unit) with the means for discharge of such waste water.

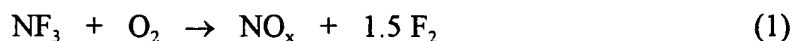
[0024] Even when a large volume of CVD exhaust gas contains NF_3 , this NF_3 can be removed with high efficiency since the thermal oxidative decomposition of exhaust gas of the present invention occurs at high temperature so that treatment can be carried out during a short time period. Moreover, operational costs are lower than the dry adsorption method since treatment is efficiently carried out using electricity (for heating), air, NH_3 , nitrogen, cooling water (including scrubbing water), etc.

[0025] The exhaust gas treatment apparatus of the present invention can be equipped with control devices to appropriately determine treatment conditions during the above mentioned consecutive treatment steps so that the treatment steps are carried out automatically. Such control devices are normally connected to detection devices (such as temperature, pressure, water level, etc. sensors) so that safe and optimum treatment is always carried out.

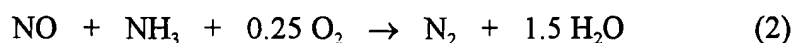
[0026]

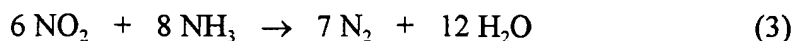
[Operation of the Invention] NO_x and F_2 are generated by oxidative decomposition reactions when NF_3 is fed to the thermal oxidative decomposition apparatus.

[0027]



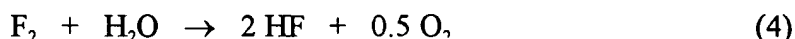
NO_x is detoxified by reaction with NH_3 to form N_2 and H_2O .





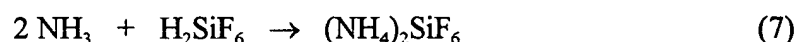
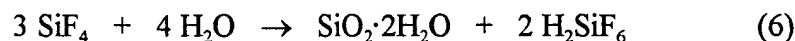
Moreover, although in the absence of NH_3 , thermal oxidative decomposition of NF_3 generates F_2 then forms the acidic derivative HF upon dissolving in water, neutralization takes place when NH_3 is present.

[0028]



Although SiF_4 , which is also contained within the cleaning exhaust gas, generates acidity upon dissolving in water, NH_3 neutralizes this acidity.

[0029]



Therefore the scrubbing water becomes acidic if the number of moles of NH_3 is not at least 4 times that of NF_3 and at least 4/3 times that of SiF_4 .

[0030] Furthermore, although reactions (1), (2), and (3) are extremely rapid above 900 °C, NH_3 itself undergoes partial oxidation above 1000 °C. Therefore treatment above 900 °C and below 1000 °C is effective.

[0031]

[Working Examples] Although the present invention is explained below by the use of working examples, the present invention is not limited to these working examples. As shown in **Figure 1**, a specific example of the exhaust gas treatment apparatus of the present invention is thermal oxidative decomposition apparatus 1. The major components of thermal oxidative decomposition apparatus 1 are exhaust gas feed section 2, reactor section 3, and discharge section 4.

[0032] Exhaust gas feed section 2 comprises exhaust gas feed line 5, nitrogen feed line 6, and air feed line 7. These feed lines form a three-layer concentric structure. NH_3 feed line 8 is connected to exhaust gas feed line 5.

[0033] Reactor section 3 comprises gas phase reactor 9 and water scrubber 10. Ceramic heater 11 is provided at the exterior wall as a heat source in order to carry out thermal oxidative decomposition of the exhaust gas within the mixed gas fed from the gas feed section, and reactor section 3 is equipped with thermocouples 12 and 13. Water scrubber 10 is provided as a following stage after gas phase reactor 9. Cooling water 14 is supplied to water scrubber 10.

[0034] Discharge section 4 comprises discharge water line 15 (discharges scrubbing waste water)

and exhaust line 16 (vents treated gas). Item 17 is a gas sampling line, and item 18 is a gas sampling line. The exhaust gas treatment of the present invention is carried out as described below using the above mentioned apparatus.

[0035] NH_3 is added via the NH_3 feed line to the NF_3 -containing exhaust gas within exhaust gas feed line 5. Nitrogen flows from nitrogen feed line 6, and air flows from air feed line 7. These gas feeds are released together into gas phase reactor 9. Substances within the exhaust gas that are capable of thermal oxidative decomposition undergo thermal oxidative decomposition. In particular, NO_x derived from NF_3 reacts with NH_3 to form nitrogen and water so that NO_x is detoxified. Remnant SiO_2 , etc. fine particles, NH_3 , F_2 , SiF_4 , etc. are removed by cooling water in the water scrubber 10 that follows reactor section 3. Solids are removed by physical entrapment. Water soluble gases are removed by dissolution, followed by neutralization by reaction with NH_3 . These removed materials are discharged through discharge water line 15. Furthermore, the detoxified treated gas is discharged through exhaust line 16.

[0036] Working Example 1

A treatment experiment was carried out using the thermal oxidative decomposition apparatus shown in **Figure 1**. Exhaust gas (NF_3 diluted to a concentration of 5,000 ppm by N_2 gas) was fed at a rate of 20 liters per minute to the exhaust gas feed line. NH_3 was added at rates that were increased step-wise. Treatment results are shown in **Table 1**. Moreover, other feeds to the thermal oxidative decomposition apparatus were as follows: air flow was 10 liters per minute, nitrogen flow was 10 liters per minute, and cooling water flow was 4 liters per minute. The gas phase reactor temperature was 950 °C. The scrubbing waste water was slightly alkaline: at least 20,000 ppm NH_3 concentration.

[0037]

[Table 1]

Feed Gas Stream		Discharge Gas			
NF_3 (ppm)	NH_3 (ppm)	NF_3 (ppm)	NH_3 (ppm)	NO_x (ppm)	F_2 (ppm)
5,000	0	40	—	2,300	< 1
5,000	5,000	30	< 1	1,500	< 1
4,900	10,000	22	< 1	480	< 1
4,900	15,000	13	< 1	75	< 1
4,900	20,000	3	< 1	2	< 1
4,900	25,000	7	< 1	1	< 1

[0038] Working Example 2

TEOS was used as a CVD process gas. NF_3 was used as a cleaning gas. Results of treatment of exhaust gas from a single-wafer type CVD apparatus are shown in **Table 2**.

[0039] Exhaust gas flow rate was 20 liters per minute so that the NH_3 concentration was 20,000 ppm. Other treatment conditions were that same as those of Working Example 1. The scrubbing water pH range was 7.0 to 10.5.

[0040]**[Table 2]**

(units: ppm)

No.	NF ₃		SiF ₄		F ₂		C ₂ H ₅ OH		CH ₃ CHO		CO		NH ₃
	in	out	in	out	in	out	in	out	in	out	in	out	out
1	3,100	8	910	< 1	800	< 1	180	< 10	85	< 10	1,500	620	< 1
2	500	4	82	< 1	< 1	< 1	2,300	< 10	100	< 10	6,700	2,400	< 1
3	4	< 1	95	< 1	< 1	< 1	1,200	< 10	330	36	2,900	1,050	< 1
4	5,300	10	410	< 1	240	< 1	300	< 10	150	15	2,300	750	< 1
5	1,100	5	56	< 1	2	< 1	45	< 10	13	< 10	200	30	< 1
6	7,200	25	200	< 1	50	< 1	340	< 10	160	20	3,300	1,200	< 1

[0041]

[Results of the Invention] Although CVD exhaust gas and cleaning exhaust gas used by a single-wafer type CVD apparatus are frequently discharged without complete separation from one another and without discharge, the present invention always performs good treatment since both types of exhaust gas (CVD exhaust gas and cleaning exhaust gas) are treated in the identical apparatus. *[TRANSLATOR'S NOTE: The phrase "without discharge" appears to be an error in the source text.]*

[0042] Concentration of NF₃ in the exhaust gas of a single-wafer type apparatus varies greatly. Per the method of the present invention, NH₃ must always be added in a manner corresponding to the maximum concentration. Although NH₃ is sometimes in excess, excess NH₃ is removed and adsorbed by water scrubbing so that exhaust gas of the thermal oxidative decomposition apparatus does not contain NH₃. Furthermore, although the scrubbing solution becomes weakly alkaline, corrosion is not a problem.

[Simple Explanation of the Illustrations]

[Figure 1] This drawing is used to explain a working example of the exhaust gas treatment apparatus of the present invention.

[Explanation of Items]

- 1 Thermal oxidative decomposition apparatus
- 2 Exhaust gas feed section
- 3 Reactor section
- 4 Discharge section
- 5 Exhaust gas feed line
- 6 Nitrogen feed line
- 7 Air feed line
- 8 NH₃ feed line
- 9 Gas phase reactor
- 10 Water scrubber

- 11 Ceramic heater
- 12 Thermocouple
- 13 Thermocouple
- 14 Cooling water
- 15 Discharge water line
- 16 Exhaust line
- 17 Gas sampling line
- 18 Gas sampling line

[Figure 1]

